

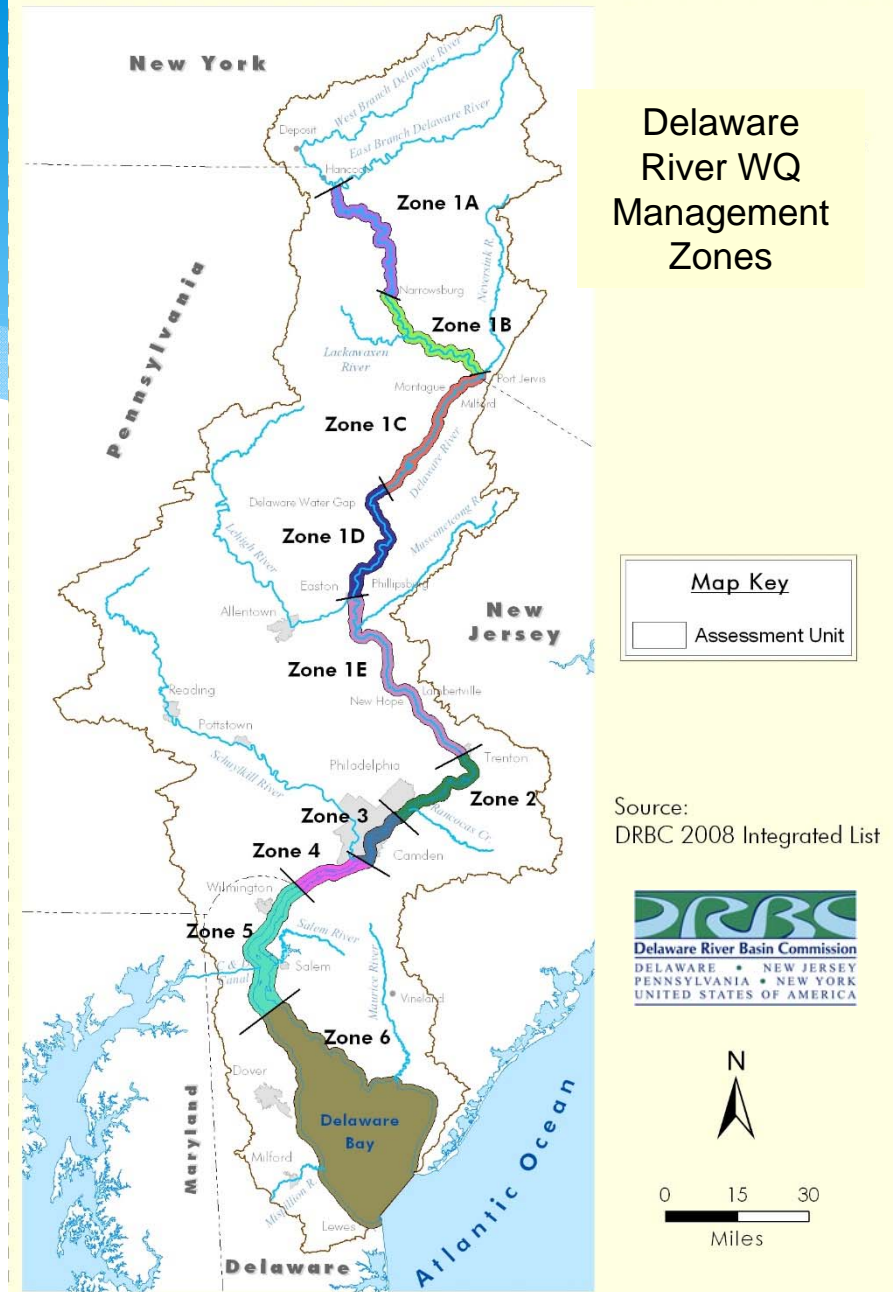
Delaware River Basin Commission

Ammonia Criteria for the Interstate Waters of the Delaware River

Toxics Advisory
Committee

January 6, 2016

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Outline

- ① Current DRBC Regulations re Ammonia
- ② Technical Background
- ② 2013 National Criteria
- ③ Ammonia Criteria Issues
- ④ Recommendations

Current DRBC Regulations

□ Article 3 Water Quality Standards

- **No** ambient or effluent requirements either basin-wide or for individual Zones in Article 3.
- Anti-degradation Existing Water Quality Parameters (Zones 1A to 1E):
 - Ammonia and Ammonium – means range between 15 to 41 $\mu\text{g/L}$ from Hancock, NY to Delaware Water Gap.
 - Ammonia – medians range between <50 and 50 $\mu\text{g/L}$ from Portland, PA to Trenton, NJ.



Current DRBC Regulations

- Best Demonstrable Technology (BDT) 30 average effluent quality of 1.5 mg/L of Ammonia-N.

□ Article 4 Application of Standards - do contain effluent requirements for ammonia

- Section 4.30.5 – Other Substances in Effluents
 - In non-tidal waters, not to exceed a 30 day average of 20 mg/L as nitrogen.
 - In tidal waters, not to exceed a 30 day average of 35 mg/L as nitrogen.



Technical Background

☐ Ammonia in aqueous solutions exists as two forms:

- ✓ NH_3 or un-ionized ammonia, and
- ✓ NH_4^+ - ammonium ion
- ✓ The proportion of each depends on the pH and equilibrium constant pK which is dependent on temperature.

☐ Ammonia speciation also depends on ionic strength, but in freshwater, this effect is much smaller than pH and temperature and was not considered in developing the criteria.

Technical Background

☐ pH Dependence

- Considerable evidence indicates that the effects of pH on ammonia toxicity is due to the joint toxicity of un-ionized ammonia and the ammonium ion.
- At very high and low pHs, pH can affect membrane function and other physiological processes that could alter ammonia toxicity.

☐ Temperature Dependence

- Invertebrate criteria are dependent on temperature, being more sensitive at higher temperatures.

Technical Background

☐ Temperature Dependence

- Since the most sensitive genera for acute toxicity are invertebrate species, the criteria are both pH and temperature dependent.
- Fish acute criteria are not dependent on temperature; but below a temperature of 15.7°C, fish are more sensitive than invertebrates. At temperatures below 15.7°C, the CMC is therefore capped at 24.1 mg TAN/L.

Technical Background

☐ Temperature Dependence

- Since the most sensitive genera for chronic criteria are invertebrate species, the criteria are both pH and temperature dependent.
- Below a temperature of 7°C, fish are more sensitive than invertebrates. Therefore, at temperatures below 7°C, the CMC is capped at 4.6 mg TAN/L.

New Data Used in Criteria Recommendations

- ❑ The 2013 update EPA conducted a new literature search and reanalyzed data considered in the 1999 update and draft 2009 criteria.
- ❑ 69 genera are now represented for acute toxicity vs 34 genera in the 1999 update.
- ❑ ~½ of the genera are invertebrates.
- ❑ The four most sensitive genera in acute tests are all bivalve mussels.
- ❑ Included acute tests with glochidia.

New Data Used in Criteria Recommendations

☐ Acute Criteria:

- The top 4 species with the lowest GMAV are all mussels.
- Data is also available for the endangered shortnose sturgeon and dwarf wedgemussel.

☐ Chronic Criteria

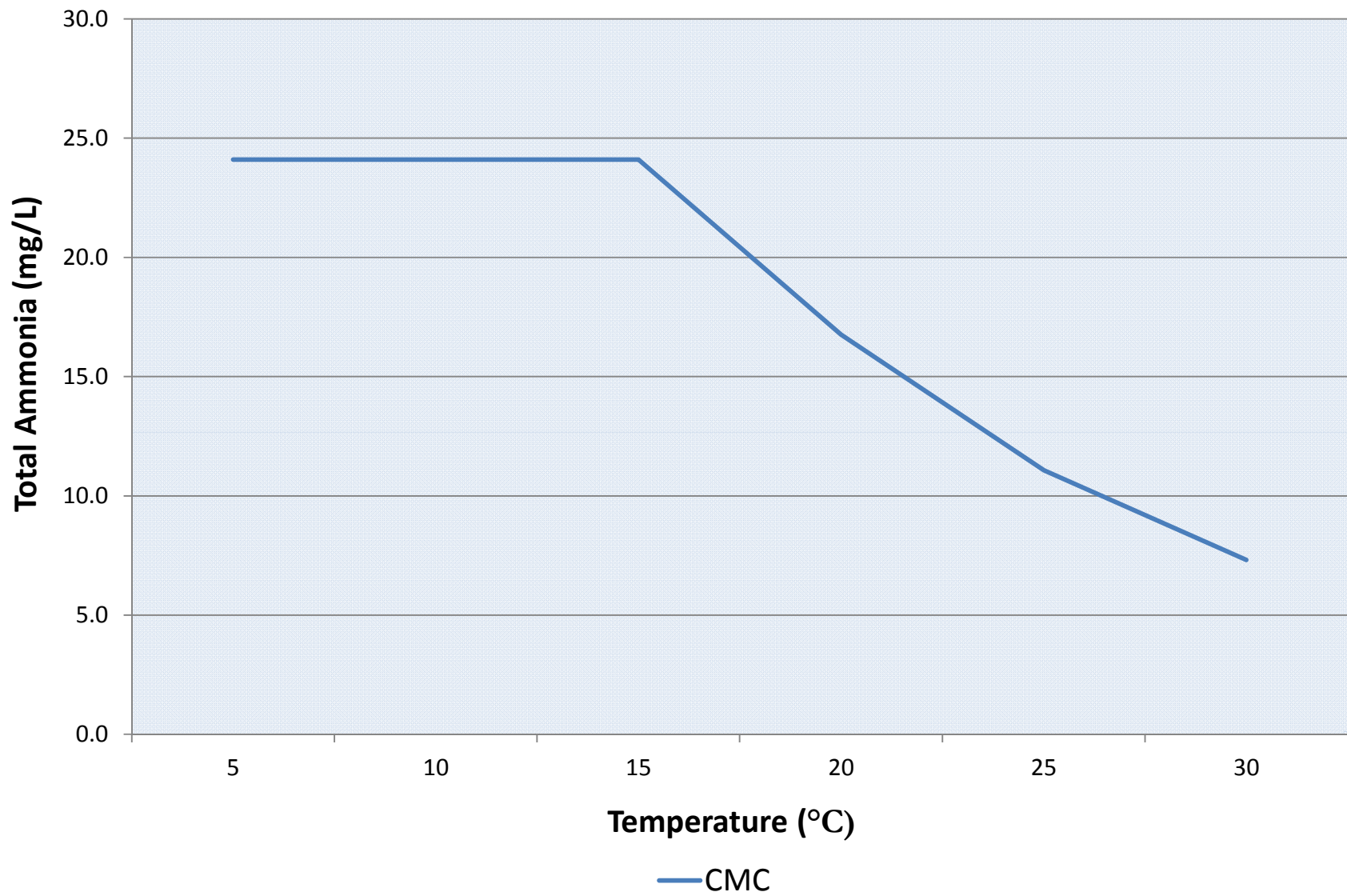
- Chronic values for 16 genera were available.
- The top 4 genera with the lowest GMCVs include two mussel, one fish and one clam.

Updated Acute Criteria

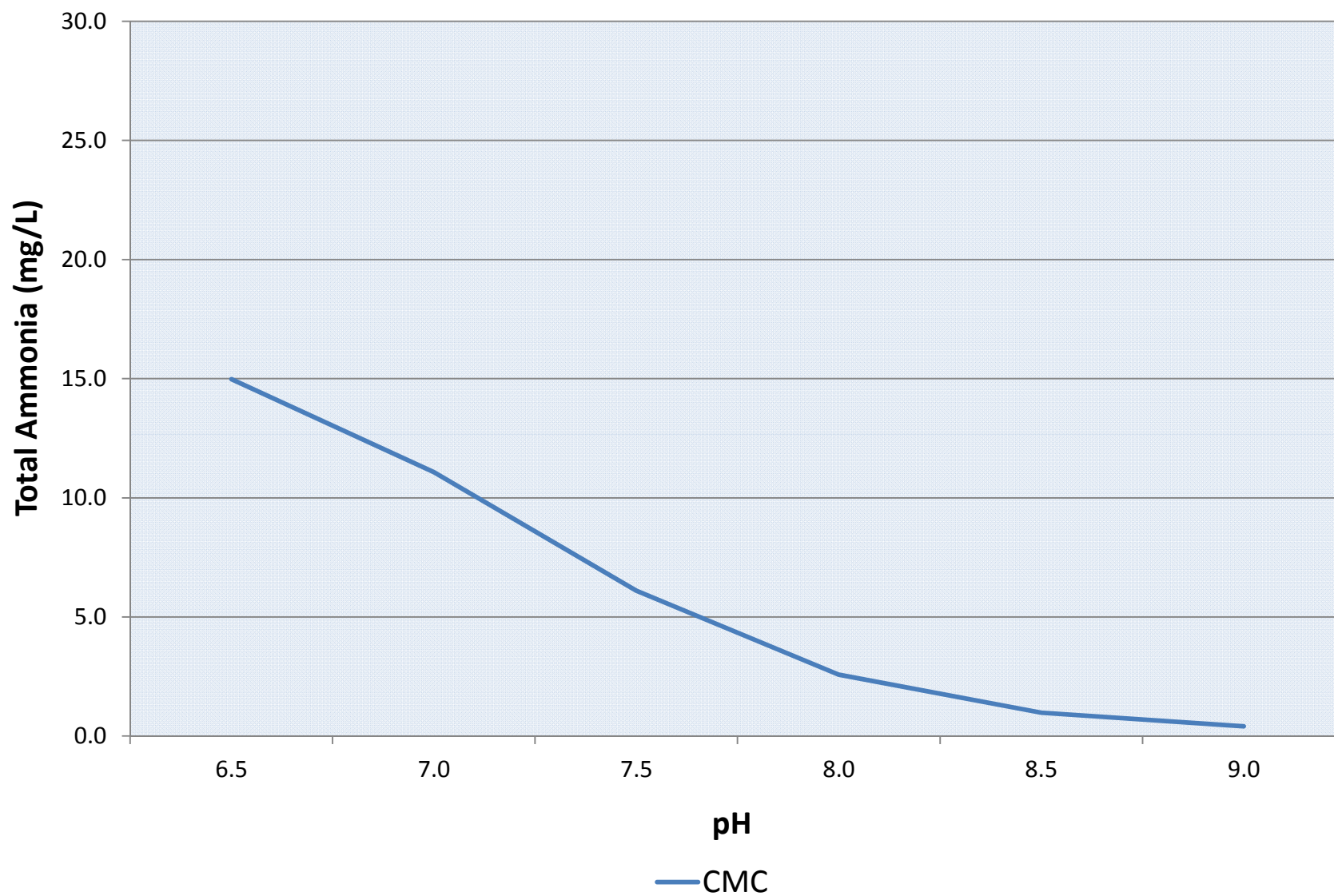
Class	Criteria (mg/L – Total Ammonia)	Value at pH=7 and T=20°C
Full Equation	$\text{CMC} = \text{MIN} \left[\left(\frac{0.275}{1 + 10^{7.204 - \text{pH}}} + \frac{39.0}{1 + 10^{\text{pH} - 7.204}} \right), \left(\frac{0.7249}{\left(\frac{0.0114}{1 + 10^{7.204 - \text{pH}}} + \frac{1.6181}{1 + 10^{\text{pH} - 7.204}} \right)} \right) * (23.12 * 10^{0.036 * (20 - T)}) \right]$	17.0
<p>Note: At low temperatures, invertebrates are less sensitive than fish so CMC is capped at 24.1 mg TAN/L at a temperature of 15.7°C and a pH of 7.0.</p>		

Ammonia Criteria Values for CMC (mg/L)

Temperature Effect, pH = 7



Ammonia Criteria Values for CMC (mg/L)
pH Effect, Temperature = 25°C

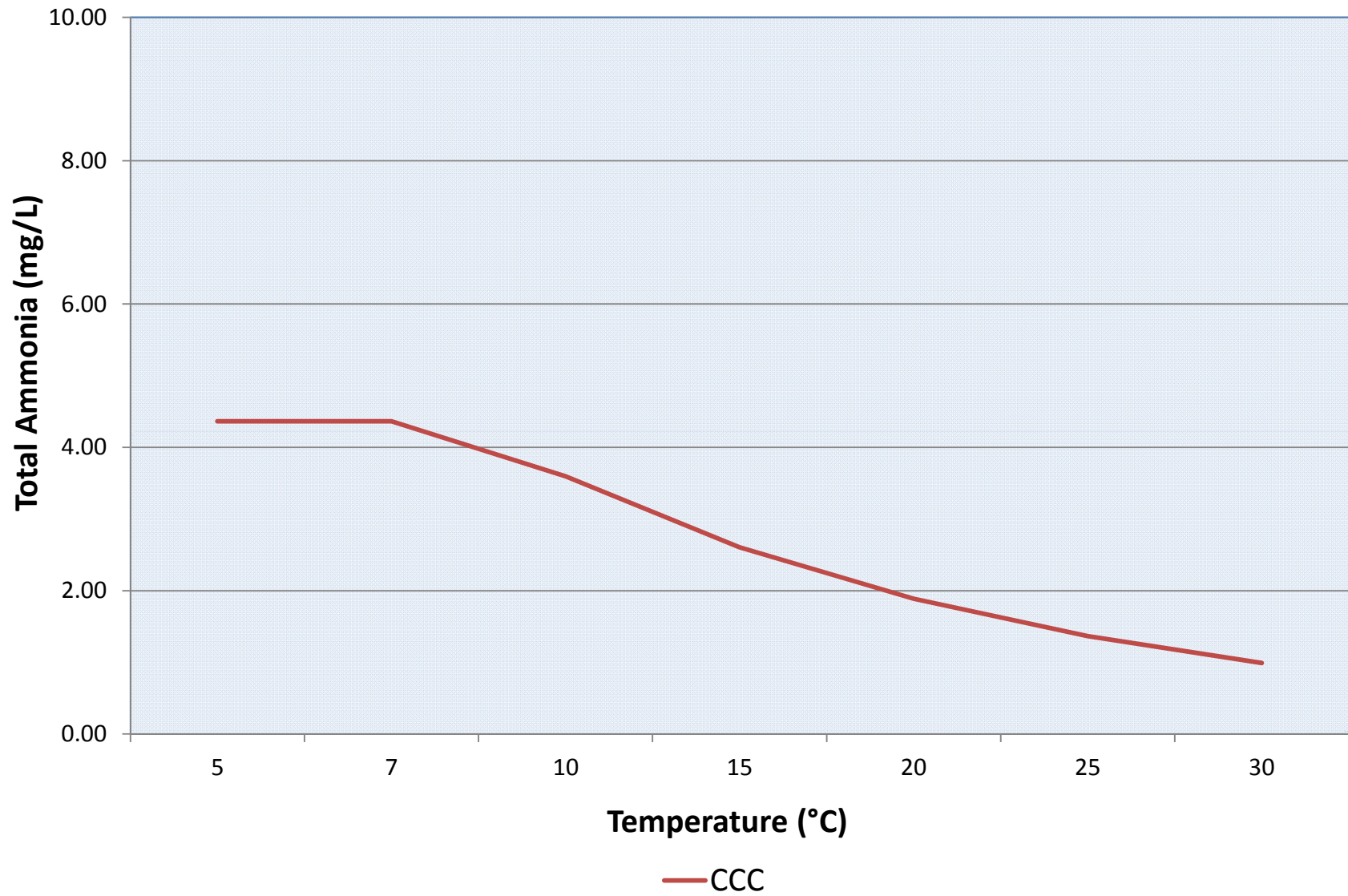


Updated Chronic Criteria

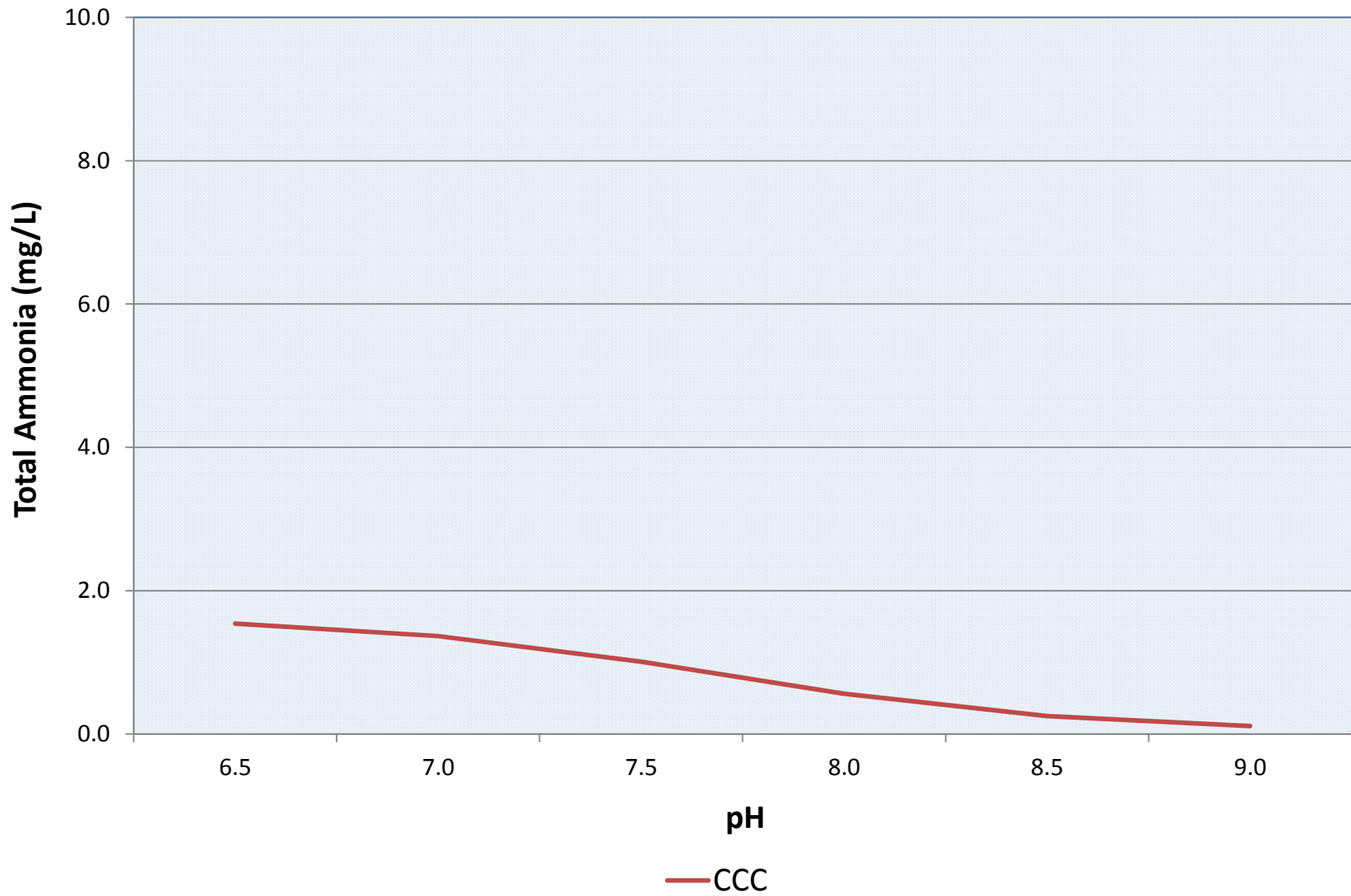
Class	Criteria (mg/L – Total Ammonia)	Value at pH=7 and T=20°C
Full Equation	$CCC = 0.8876 * (0.0278 / (1 + 10^{(7.688 - pH)}) + 1.1994 / (1 + 10^{(pH - 7.688)})) * (2.126 * 10^{(0.028 * (25 - \text{MAX}(T, 7)))})$	1.9
Additional Requirement	Not to exceed 2.5 times the CCC as a 4 day average within the 30 day duration more than once every 3 years.	4.8

Ammonia Criteria Values for CCC (mg/L)

Temperature Effect, pH = 7



Ammonia Criteria Values for CCC (mg/L)
pH Effect, Temperature = 25°C



Ammonia Criteria Issues

- ❑ Need uniform criteria for shared waters.
 - States are considering options for state-wide adoption of the new criteria.
 - Implementation policies utilized by states could result in differing criteria.
 - Differing criteria hampers cumulative assessment of multiple discharges.

Ammonia Criteria Issues

□ Application of criteria:

- pH data or value to be used.
- Temperature data or value to be used.
- Design flows

Preliminary Staff Recommendations

☐ Acute Criteria:

- Adopt 2013 EPA recommended freshwater acute criteria formulas for total ammonia for Zones 1 through Zone 5 (above RM 68.75).
- Criteria are related to pH and temperature.
- Assume mussels are present in Zones 1 through 5 given the DRBC biosurvey data in Zone 1 and the PDE data in Zones 2 – 5.
- Duration of criteria – 1 hour

Preliminary Staff Recommendations

☐ Chronic Criteria:

- Adopt EPA recommended chronic criteria formulas for **total ammonia**.
- Criteria are related to both pH and temperature.
- Duration – adopt both 30 day average criteria formula and the 4 day average criterion value.

Preliminary Staff Recommendations

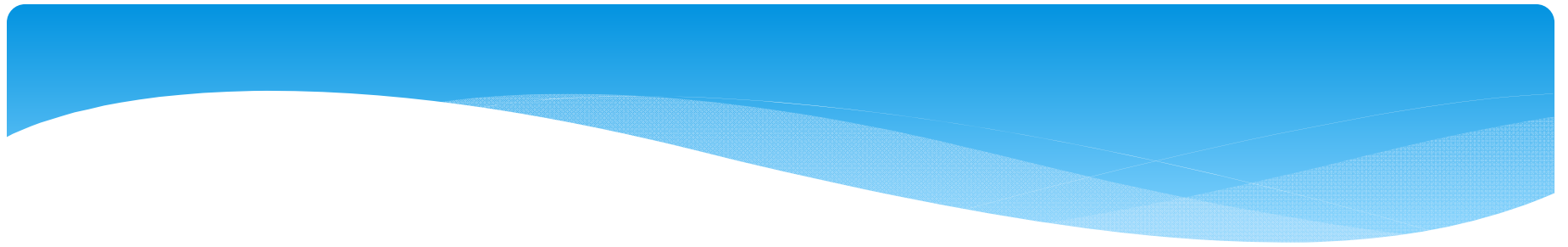
□ Application of Standards:

- Duration – Follow EPA recommendations.
- pH and temperature values – options are:
 1. Utilize site-specific data typically from automatic monitors (for all or specified Zones).
 2. Specify a median pH value of 7.1 (Section 4.20.5A3.) and background temperature specified in Section 4.30.6C.1. for Zones 2, 3 and 4.
 3. Specify a percentile from a frequency distribution of data.

Preliminary Staff Recommendations

□ Application of Standards:

- pH and temperature values – options are:
 - 4. Specify median pH values for Existing Water Quality (EWQ) at Interstate Control Points (ICPs) in Special Protection Waters in Zones 1A-1E [Section 3.10.3A.2.g.3)].
- Design Flows: per Section 4.30.7B.2.c.b)
 - Acute Criteria – 2500 cfs at Trenton and 7Q10 for other tributaries.
 - Chronic Criteria – 30Q5 flow at both Trenton and for other tributaries.



Marine Criteria for Ammonia

- ❑ Only three of the five signatory parties have water quality criteria for un-ionized ammonia. PA and DE do not have criteria.
- ❑ EPA and NY have the same criteria. NJ's criteria are somewhat lower.
- ❑ Total ammonia criteria vary depending on the pH, temperature and salinity. U.S. EPA (1989) provides conversion tables. Total ammonia criteria are lower at higher salinities.

Federal/State Marine Criteria Comparisons

Agency	Class	Acute (mg/l)	Chronic (mg/l)
U.S. EPA (un-ionized)		0.233	0.035
DE	-	-	-
NJ (un-ionized)	SE	0.115	0.030
	SC	0.094	0.024
PA	-	-	-
NY (un-ionized)	SA, SB, SC, I, SD	0.23	-
	SA, SB, SC, I	-	0.035

Recommendations

- ☐ Determine the basis for the differences between NJ's and national criteria.
- ☐ Continue discussion of appropriate criteria at the next meeting of the subcommittee.